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POLE-EFFECTS, PRESSURE-SHIFTS, AND MEASUREMENTS OF WAVE-LENGTH IN THE SPECTRUM OF MANGANESE

A DISSERTATION

SUBMITTED TO THE FACULTY
OF THE OGDEN GRADUATE SCHOOL OF SCIENCE
IN CANDIDACY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS

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GEORGE SPENCER MONK

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ABSTRACT

Interference measurements in the arc spectrum of manganese between λ 4470 *and* λ 6021.—Pole-effects, pressure-shifts, and wave-lengths for the stronger lines of manganese between λ 4470 and λ 6021 have been measured. A carbon arc with the lower, positive, pole bored out and filled with manganese dioxide was used as a source. (1) *Pressure-shift:* The interference method used does not seem to be suitable for observations on pressure-shift in manganese, on account of the intrinsic wideness of many lines, and their widening under pressure. The evidence obtained indicates a correspondence between unsymmetrical broadening of the lines under pressure, and pole-effect. (2) *Pole-effect:* Little or no pole-effect is observed with a carbon arc whose lower pole is filled with manganese chloride. There are objections, however, to its use. A moderate effect is observed at the positive pole of a carbon arc filled with manganese dioxide, and a larger effect with an arc between metallic poles. (3) *Wave-lengths:* Only about 1 millimeter of the center of a 12 mm to 15 mm, 5-ampere arc on a 220-volt circuit was used, and it is believed that pole-effect is entirely absent from the measurements. The wave-lengths of about forty lines have been measured with an accuracy estimated at 0.002 A. Lines of neon and lines of iron of group *a* were used as standards, the strongest component of Hg 5461 serving as an auxiliary standard.

On account of the prevalence of manganese as an impurity in iron, and the consequent appearance in the spectrum of iron of the stronger manganese lines, the spectrum of manganese is of interest as a possible source of standards of wave-length. Also, a knowledge of the correct wave-lengths of many manganese lines is necessary for comparison with the corresponding wave-lengths in the sun. This paper contains the results of interferometer measures of the wave-lengths of a number of lines in the region λ 4470 to λ 6021, together with an examination of the stronger lines in that region for pole-effect, and their behavior under moderate differences of pressure.

Wave-lengths of manganese lines have been published by a number of observers. Chief among these are those due to Exner and Haschek,[1] Kilby,[2] and Fuchs,[3] while some of the stronger lines

[1] *Die Spektren der Elemente*, Leipzig, 1912.

[2] *Astrophysical Journal*, 30, 243, 1909.

[3] *Zeit. für Wiss. Phot.*, 14, 239, 1915.

have been measured as impurities in the arc spectrum of nickel by Hamm,[1] and of iron by Burns,[2] who used the interference method.

THEORY AND APPARATUS

From elementary theory, it is easily deduced that the fractional order of interference at the center of the ring system formed by the passage of light through a parallel-plate interferometer is expressed by

$$E+(n-1)=\frac{D_{n-1}^2}{D_n^2-D_{n-1}^2}(1+D_n^2/8F^2m^2), \qquad (1)$$

where E is the fractional part of the whole order of interference at the center of the ring system, D is the diameter of a ring, F is the focal length of the lens or mirror projecting the fringes on the slit of a spectrograph, m is the magnification of the spectrograph, and n is an integer referring to the number of the ring counting from the center outward. This equation holds only when the magnification of the spectrograph is constant for all wave-lengths. For the apparatus used in this investigation, F is 500 mm, the maximum D is 25 mm, and m is 1.07. Hence, neglecting the second term in the bracketed factor on the right-hand side of equation (1) introduces a negligible error of one part in about thirty-five hundred for the largest fringe measured. Also, it can easily be shown that the difference between the squares of the diameters of contiguous fringes for a given wave-length is a constant. Hence, equation (1) can be put into the simpler form

$$E+(\text{integer})=\frac{D^2}{D_k^2-D_{k-1}^2} \qquad (2)$$

in which the denominator is the average of all the differences of diameters squared for a given line. Thus, by the use of equation (2), as many determinations of E, the fractional order of interference at the center of the ring system for a given line, may be made as the number of fringe diameters measured. In practice, this number was limited to eight or nine. Equation (2) is due to St. John and Babcock, and its use has been explained by them.

[1] *Zeit. für Wiss. Phot.*, 13, 105, 1913. [2] *Ibid.*, 12, 207, 1913.

The conditions in the foregoing theory are present in the apparatus used. Light from a source L (Fig. 1) is focused on the aperture of a parallel-plate interferometer by a concave mirror C_1, of 17 cm diameter and 60 cm focal length. By means of a plane mirror M, the light is then reflected to concave mirror C_2, which is set at a distance from the slit S equal to its focal length. Thus the fringes produced at the interferometer are in focus on the slit. For most of the plates, C_2 is of 50 cm focal length, although some were taken with mirrors of 60 cm and 25 cm focal length. Auxiliary

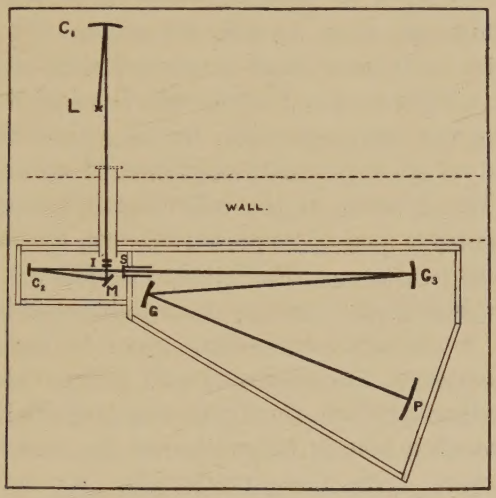

FIG. 1

dispersion of the fringes for different wave-lengths is obtained by the use of a concave grating G, on which the incident rays are made parallel by the use of the concave mirror C_3, of approximately 6 meters focal length. This form of the apparatus is due to Pfund. The grating, ruled by Professor Michelson, is of good quality and has a ruled surface 2 inches by 5.5 inches, with 15,000 lines to the inch. Its focal length is 21 feet. A negligible amount of astigmatism exists in the spectrograph owing to the small angle, about two degrees, between the incident and reflected beams at C_3. The grating and plate-holder are mounted at the ends of a rigid steel bar, which is movable about a vertical axis passing through the

center of the grating. The photographic plate is 10 inches long by 2 inches wide, bent so that the fringes are in focus over its entire length. The plate-holder is so mounted in guides that it can be moved a small distance horizontally in a direction at right-angles to the beam of light by means of a push-screw, thus permitting exposures, with the source under different conditions, to be photographed so that the spectrum lines are side by side on the same plate. The housing of the auxiliary spectrograph is large enough to permit exposures in the yellow of the second order.

The interferometer is equipped with a number of etalons ranging in thickness from 2.5 mm to 40 mm. The etalons are brass rings with three invar studs exactly equal in length to within a fraction of a light-wave. During this investigation, a pair of quartz mirrors was used, accurately flat to a fraction of a fringe, and sputtered to an appropriate thickness of silver by cathodic deposition. The aperture of the interferometer, upon which the light of the source is focused, is placed between the source and the silvered surfaces, and as near the latter as possible.

The entire instrument, inclosed in a tight, double-walled box, is located in a constant-temperature room in the basement of Ryerson Laboratory. The source of light and the concave mirror C_1 are in an adjoining room, the light being projected on the interferometer through a hole in the wall, over one end of which is a plate-glass cover. With these precautions, the interior of the interferometer box and spectrograph is free from temperature effects sufficient to cause displacements of the fringes. In order to obtain a check on instrumental changes of any sort during exposures, a short exposure to a Cooper-Hewitt lamp was made on each plate before and after each of the principal exposures. In addition, the order in which the exposures to manganese arc and standards were made was varied, to prevent systematic errors due to possible changes. Some few plates were taken with simultaneous exposures of manganese and standard source, but it was found that successive exposures with the Hg spectrum as a check gave satisfactory results. It might be mentioned in this connection that the character of the lines examined made the highest degree of accuracy of measurement impossible. Where the character of the inter-

ference fringes and the nature of the source permit the greatest accuracy, simultaneous exposures are to be recommended.

In all, about fifty plates of the manganese spectrum were taken and measured. The source was a vertical carbon arc, mounted so that quick and accurate adjustments could be made for focus and setting of the image of the source on the interferometer aperture. In the lower, positive, electrode, about 12 mm in diameter, was drilled a 3 mm hole, packed with MnO_2. The upper, negative, electrode was a solid carbon, 9 mm in diameter. Attempts were made to use a metallic manganese arc, in the hope that the extremely steady conditions of the Pfund iron arc could be obtained, but metallic manganese spluttered so badly that it proved unmanageable. Some exposures were made with a carbon arc as described, the lower pole being charged with manganese chloride instead of manganese dioxide. This arc required too frequent charging, and the location of the center of the arc was an uncertain matter. The manganese dioxide formed a bead almost equal in steadiness and longevity to the bead of the Pfund iron arc. The current was maintained at 5 amperes on a 220-volt circuit, and the distance between the electrodes was from 12 to 15 mm.

For the red region, Wratten Panchromatic plates were used. Cramer old-style X-ray plates, having a pronounced maximum of sensitiveness to the green, were used for wave-lengths below λ 5600. Exposure times ranged from about four minutes for the brightest component of Hg λ 5461 to an hour for some of the faint lines of manganese.

The etalons used were 5 mm and 7.5 mm. The choice of these distances rather than distances with a greater difference between them was necessitated by the character of the lines measured. Most of them were intrinsically very wide. The principal effect of the small range is an increase of the uncertainty of the phase-change correction. A comparison of the measures with those of other observers indicates that no systematic error has been thus introduced.

The image of the source in focus on the interferometer was about 5.5 times the size of the source. This gave an image of the arc between 70 and 80 mm in length. The aperture of the interferometer was rectangular in shape, and 6 mm high by 13 mm wide.

Thus, the central portion of the arc selected was well within the dimensions prescribed by the Committee on Standard Wave-Lengths. The interferometer was so placed that an image of its aperture coincided with the ruled area of the grating and was in sharp focus thereon. It is believed that on account of the large magnification of the arc, and the careful selection of its center, the wave-lengths determined are entirely free from pole-effect.

MEASUREMENT AND COMPUTATION

The plates were measured on a Gaertner comparator, readings being made to hundredths of a millimeter. Two or three settings were made and averaged for each fringe. In some exceptional cases, such as in preliminary determinations of the phase-change correction where the etalon used was so small that a mirror of comparatively short focal length was used to project the fringes on the slit, the readings were made to thousandths of a millimeter. From the measured diameters of the fringes, the fractional orders of interference were computed to the third decimal place according to formula (2). The integral part of the order of interference was computed on a calculating machine by a quick and easy method similar to that described by Meggers. The complete order of interference thus obtained, multiplied by the wave-length of the standard line, gave the double distance between the interferometer plates. This value, divided by the orders of interference for the other lines on the plate, gave the wave-lengths of those lines to the fourth decimal place.

As standards, in the red, lines of neon were used, in particular λ 5944.834; in the green, the Fe line λ 5497.522 was used as a standard, although many of the plates were measured in terms of Hg λ 5461, this line being measured in terms of the Fe and neon lines for both etalons. The adopted values of the wave-length of the bright component of Hg λ 5461 were: for the 5 mm etalon, λ 5460.7443; for the 7.5 mm etalon, λ 5460.7434. The difference is due to a greater nearness of a fainter component for one of the etalons. Both of these values are slightly larger than the value λ 5460.7424 obtained by Fabry and Buisson with a 5 mm etalon. A number of plates were taken with neon, mercury, and iron, giving a check on the phase-change corrections used. A curve

plotted for the corrections thus derived agrees well with that obtained from the manganese measures. In compiling the final table of wave-lengths, the formula for the phase-change correction derived by Meggers was used. Table I shows the application of the formula to three lines and a comparison with the values obtained by calculating the phase-change correction for the region on the basis of the neon lines, assuming the Bureau of Standards values as correct.

TABLE I

REDUCTION FOR PHASE-CHANGE

$\Delta_1=\frac{e_2 c}{e_2-e_1}$; $\Delta_2=\frac{e_1 c}{e_2-e_1}$; $e_1=5.0$ mm; $e_2=7.5$ mm

c=difference between uncorrected wave-lengths of a line for two etalons

LINE	UNCORRECTED		c	CORRECTED	BY NEON LINES	ADOPTED
	7.5 mm	5.0 mm				
6013.....	.4964	.4978	−0.0014	.4936	.4946	.494
6016.....	.6459	.6474	−0.0015	.6432	.6440	.644
6021.....	.8015	.8028	−0.0013	.7987	.7995	.799

PRESSURE-SHIFTS

Table II gives the results of measures on a number of lines photographed with the source subject to pressures ranging from 5 cm to 160 cm of mercury. A plate taken with a metal electrode showed fringes so widened for moderate pressures that measures were impossible. It was not considered advisable to make a more comprehensive study of pressure-shifts in manganese at this time in view of the small extent of the region investigated.

TABLE II

Line	Displacement per Atmosphere High-Low	Line	Displacement per Atmosphere High-Low	Line	Displacement per Atmosphere High-Low
4709.....	0.004	4783.....	0.004	5470.....	0.007
4727.....	0.004	4823.....	0.006	5481.....	0.008
4739.....	0.002	5341.....	0.004	5516.....	0.003
4754.....	0.006	5377.....	0.008	5537.....	0.008
4761*	0.014	5394.....	0.006	6013.....	0.009
4762	0.006	5399.....	0.009	6016.....	0.011
4765*	0.009	5420.....	0.010	6021.....	0.013
4766	0.006	5432.....	0.003		

* Close pairs, measures doubtful.

It is important to note a fact which does not appear from Table II. The displacements for λ 4754, λ 4783, and λ 4823 are from settings on what appears to be the center of the most dense portion of the fringes. Actually, in pressures higher than atmospheric, these fringes were drawn out so far toward the center of the ring system for each of the lines that it was doubtful where the center of the line really lay. In other words, these three lines were unsymmetrically widened toward the red, a condition frequently noted in certain groups of lines photographed under high pressures, and strikingly illustrated in the plates of Gale and Adams[1], taken with the source under a pressure of 8 atmospheres. The displacements indicated in Table II for λ 6013, λ 6016, and λ 6021 are based on observations at atmospheric pressure or less, no measures being made on plates taken at higher pressures.

POLE-EFFECT

The pole-effect for manganese has been investigated by Brendel-Wirminghaus[2] for wave-lengths shorter than λ 5600. This investigator used a carbon arc, one pole drilled out and filled with manganese chloride. She concluded from her results that the spectrum of manganese showed no pole-effect. The present writer made a number of exposures with this form of arc, and observed little or no pole-effect at the negative, carbon, pole. At the positive pole, which was drilled out and filled with manganese chloride, the results were inconclusive, a few plates showing an appreciable effect, and many, none at all. An objection to the use of manganese chloride is in the uncertain manner in which the arc burns. Most of the time, since the chloride is used up quickly, the arc issues from the positive pole at a point between 2 and 5 mm below the end of the electrode, rendering observations for pole-effect useless.

With a metallic arc, the values shown in Table III have been obtained, using the third order of the 10-inch Michelson grating in the 30-foot Littrow spectrograph. A comparison with the results of St. John and Babcock is given in Table III. Several exposures

[1] *Mt. Wilson Contr.*, No. 58; *Astrophysical Journal*, **35**, 10, 1912.

[2] *Zeit. für Wiss. Phot.*, **20**, 229, 1921.

using the interference method with a carbon arc, in which the lower, positive, pole was drilled out and packed with manganese dioxide, gave the results in Table IV.

TABLE III

Line	Monk	St. John and Babcock
	Neg. Pole-Center	Neg. Pole-Center
6013	0.018	0.019
6016	0.017	0.020
6021	0.019	0.018

TABLE IV

Line	No. Plates	Positive Pole-Center	Line	No. Plates	Positive Pole-Center
4472	1	.003	5255	2	.003
4490	1	.003	5341	2	.003
4498	1	.003	5377	2	.008
4502	1	.004	5394	3	.003
4709	3	.002	5420	3	.005
4727	3	.004	5470	3	.003
4739	3	.004	5481	3	.006
4754	2	.008	5505	2	.005
4783	2	.009	5516	4	.005
4823	2	.007	6013	4	.007
5150	2	.005	6016	4	.008
5196	2	.005	6021	4	.012

λ 4754, λ 4783, λ 4823, which were mentioned in connection with the discussion of pressure-shifts, as having an abnormal widening toward the red under pressure, are here shown to have

(*a*) (*b*) (*c*)

FIG. 2

larger pole-effects than other lines in the same region. It is also of interest, in connection with pole-effect, to notice the difference in appearance of the three types of arc used. These are illustrated

in Figure 2: (*a*) is almost uniform in intensity from pole to pole, the arc at the positive pole seeming to spring from the crater in which the manganese chloride has sunk; (*b*) has a marked condensation of the discharge at the point on the manganese oxide bead from which the arc springs, and is brighter there; (*c*) has this same feature at the positive pole, and an excessively great intensity at the negative pole.

WAVE-LENGTHS

The adopted wave-lengths for the lines measured are shown in Table V, compared with the results of other observers. A difference of 0.1 A in the case of λ 4739 is undoubtedly due to an error or misprint in the lists of other observers, since no manipulation of the whole number part of the order of interference will give an approximation to their results. The value for λ 5377 is in some doubt owing to the presence of a faint line close on the violet side. While the probable errors in column 8, based on the collected measures from each plate, are as low as 0.001 A, this does not represent the consistency of the measures of the individual fringes for a single exposure. These were not so good, especially for the very wide lines. Consequently, it is believed that claim cannot be made to greater accuracy than 0.002 A.

The usefulness of manganese lines in the region studied as possible secondary standards is in general impaired by two considerations. Many of the lines are eliminated on account of their intrinsic width. Most of those which are designated by Janicki as sharp, simple lines are as a rule most affected by pressure-shift and pole-effect. Among these latter are λλ 4754, 4783, 4823, 6013, 6016, 6021, which on account of their intensity, appear most frequently in the arc spectrum of iron. With exposures carefully made on the center of the arc, they should be useful as standards of measurement.

No lines of any prominence were measured in the region between λ 5537–λ 6013. While there are several lines of moderate intensity in the neighborhood of λ 5800, none of the plates taken showed them with sufficient density for measurement. Three other lines, λ 4709, λ 4727, and λ 4739, all sharp, and having the advantage of comparative isolation in the spectrum, gave promise of usefulness

as standards. The values obtained for these lines are however so different from the values obtained by other observers that

TABLE V

Line	Rowland	I. A. Units					Prob. Error	No. Plates
	Exner & Haschek	Kilby	Fuchs	Burns	Hamm	Monk		
4470	.33	.138	.142	.141	.147	.140	.0006	7
4472	.98	.800	.793	.....	.....	.796	.0004	7
4490	.27	.071	.078	.....	.....	.081	.0002	6
4498	.09	.898	.897	.903	.....	.900	.0004	6
4502	.40	.218	.223	.219	.228	.222	.0003	7
4605	.52	.378	.367	.....	.....	.365	.0005	6
4626	.69	.552	.546	.....	.....	.542	.0004	6
4671	.89	.694	.688	.....	.....	.684	.0008	2
4701	.31	.150	.158	.....	.....	.154	.0008	3
4709	.89	.708	.704	.....	.....	.713	.0002	11
4727	.70	.476	.462	.464	.....	.479	.0002	11
4739	.30	.004	.001	.....	.....	.106	.0002	11
4754	.24	.046	.048	.....	.....	.041	.0004	6
4761	.73	.521	.527	.524	.528	.526	.0002	6
4762	.60	.375	.375	.373	.374	.375	.....	2
4765	.08	.852	.856	.863	.861	.861	.0003	6
4766	.63	.414	.426	.422	.421	.429	.0004	5
4783	.62	.454	.432	.434	.....	.428	.0006	6
4823	.71	.521	.522	.....	.....	.516	.0006	6
5117	.10	.944	.935	.....	.....	.940	.....	1
5150	.10	.937	.....	.....	.....	.930	.....	2
5255	.48	.330	.330	.....	.....	.320	.0004	4
5341	.25	.068	.070	.....	.....	.066	.0012	7
5377	.86	.623	.634	.....	.....	.619	.0007	11
5394	.89	.679	.677	.....	.....	.676	.0006	15
5399	.70	.494	.506	.....	.....	.487	.0006	9
5407	.67	.429	.432	.....	.....	.428	.0009	4
5413	.90	.690	.696	.....	.....	.683	.0010	5
5420	.61	.371	.368	.....	.....	.361	.0007	6
5432	.75	.553	.555	.....	.....	.545	.0006	11
5457	.64	.....	.468	.....	.....	.463	.....	1
5470	.88	.644	.640	.....	.....	.642	.0005	8
5481	.61	.401	.395	.....	.....	.387	.0006	5
5505	.10	.874	.877	.....	.....	.874	.0006	9
5516	.00	.774	.773	.....	.....	.773	.0005	11
5537	.99	.753	.749	.....	.....	.759	.0007	9
5551	.20	.991	.987	.....	.....	.984	.....	1
5567	.02	.....	.764	.....	.....	.761	.....	1
6013	.74	.480	.484	.....	.....	.494	.0006	12
6016	.90	.631	.636	.....	.....	.644	.0005	13
6021	.05	.794	.787	.....	.....	.799	.0008	14

further measurement is necessary. It is planned to continue this investigation in the arc spectrum of manganese, using a cadmium

tube as a standard source, for such lines as these, for fainter lines, and for other parts of the spectrum.

In conclusion, the writer wishes to acknowledge the help and guidance of Dr. H. G. Gale, under whose direction this work was begun and carried on, and whose liberality in time and equipment made the results possible. Thanks are also given to Messrs. St. John and Babcock, who furnished details of their own apparatus, to Dr. Elias Klein for taking and measuring several plates, and to Mrs. Monk for aid in measuring and computing.

RYERSON LABORATORY
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